

Lithium-Oxygen Battery Design and Predictions

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Project ID# BAT-420

Overview

Timeline

- Start: 2018
- Finish: 2021
- **30 %**

Budget

- Total project funding
 - DOE share: \$ 1200 K
 - Contractor 0
- FY 19: \$ 500 K
- FY 20: \$ 350 K
- FY 21: \$ 350 K

Barriers

- Barriers addressed
 - Cycle life
 - Capacity
 - Efficiency

Partners

- Interactions/ collaborations
 - B. Narayanan, University of Louisville
 - F. Khalili-Araghi, UIC
 - J. G. Wen, ANL
 - A. Subramanian (UIC)
 - Y. Zhang, ANL

Project Objectives and Relevance

- The objective of this work is to advance Li-O₂ battery concepts that operate in an air environment with long cycle life and high efficiency through novel design and predictions.
- A major goal of this work is to enable operation in an air environment and thus increase volumetric energy density needed for practical applications of Li-O₂ batteries
- The focus is on discovery of new combinations of electrolytes and additives that can promote the cathode functionality of 2-dimensional transition metal dichalogenide (TMDC) catalysts that have high activity for oxygen reduction and evolution.
- Li-O₂ batteries are considered a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy
- A major focus is on increasing rates and energy densities with new materials development and combinations

FY21 Milestones

Month/ Year	Milestones
Dec/20	Use a conductive MOF for Li-O2 battery to increase the number of active sites in cathode materials based on MOFs as well as localize them in pores. Q1 (Completed)
Mar/21	Utilize new transition metal alloy catalyst for Li-O ₂ batteries that work in synergy with electrolyte to increase charge/discharging rates and carry out computations (Q2, FY 2021; Completed)
Jun/21	Investigate electrolyte additives that work with the new alloy catalyst to increase charge/ discharge rates and give anode protection with computations (Q3, FY 2021, Completed)
Sep/21	Design and synthesize new cathode materials with high surface areas to increase energy densities with computational analysis

Strategy

- The strategy is to use cathode materials based on 2-dimensional transition metal dichalcogenides (TMDCs) that we have found to be among the best oxygen reduction and evolution catalysts^{*} and have shown exceptional performance in Li-O₂ electrochemistry.
- These cathode materials will be the basis of our strategy to carry out systematic studies of electrolyte blends and additives that will reduce charge potentials and enable long cycle life.
- In the initial stages we will focus on establishing this strategy for an O₂ atmosphere and then extend to a realistic air atmosphere.
- The strategy will use integrated experimental/theoretical investigation to develop an understanding of the complex reaction mechanisms to promote high rates and long cycle life with new types of anode protection.
- New cathode materials with higher surface area will be synthesized with 3D printing and computational analysis

Experimental and computational methods

Synthesis of cathode materials

Chemical Vapor Transport method for the synthesis of bulk cathode materials; liquid phase exfoliation technique to produce nanostructured cathode materials

Characterization and Testing

DLS, AFM, TEM imaging, EDXXPS, Raman, XRD, SEM, DEMS imaging, impedance measurements, cyclic voltammetry (CV), high throughput screening, charge-discharge cycling experiments in Swagelok systems

Computation

Density functional theory (DFT), ab initio molecular dynamics (AIMD), classical molecular dynamics (CMD), periodic and cluster calculations, high throughput screening, machine learning and artificial intelligence for optimizing electrolyte/catalyst synergies



Accomplishments

A conductive metal organic framework (MOF) in combination with a redox mediator results in formation of a conductive amorphous Li_2O_2 that facilitates the growth and decomposition of the discharge product in a Li-O2 battery.

- The battery with this configuration exhibits sustainable and efficient operation with a low charge potential
- It has an extended lifetime of 100 cycles at a capacity of 2000 mAh/g under a current density of 0.2 mA/cm².

Fast charge and discharge rates with high capacities have been achieved in $Li-O_2$ batteries using a new binary transition metal dichalcogenide alloy, $Nb_{0.5}Ta_{0.5}S_2$, for the cathode and a colloidal KMnO4 electrolyte

- Due to its low work function, effective electron transfer between the Nb_{0.5}Ta_{0.5}S₂ metal edge and O₂ facilitates both oxygen reduction and evolution reactions (ORR and OER) occurring during discharge and charge processes
- An multi-functional colloidal electrolyte is found to work in synergy with the cathode to promote the fast charge and discharge rates at high capacities.
- Computational simulations have been used to provide insight into the functionalities of this new Li-O₂ battery and how they promote fast charge/discharge and anode protection



Investigation of the effect of adding electronic conductivity to a metal organic framework (MOF) on Li-O₂ battery performance: <u>Copper Tetrahydroxyquinone (Cu-THQ) structure</u>





HRTEM images of Cu-THQ nanoflakes along [001] showing an elliptical pore packing.

- MOFs) are promising platforms for cathodes owing to their ultra-high porosity, enormous surface area, highly ordered structure and tunable chemical composition.
- However, traditional MOFs are still far from practical cathode materials due to their insulator nature and have not given very good performance in Li-O₂ batteries.
- This is the first study of a conductive MOF in a Li-O₂ battery.

Investigation of the effect of adding electronic conductivity to a metal organic framework (MOF) on Li-O₂ battery performance: <u>characterization of discharge product</u>



TEM results of the cathode after the 10th discharge

EELS results of the product of the cathode after the 10th discharge

- Li₂O₂ discharge product was verified by TEM, DEMS, and EELS
- TEM image reveals the presence of of 2-5 nm sized nanocrystalline Li₂O₂ with grains embedded in amorphous Li₂O₂. Amorphous Li₂O₂ has previously been shown to have good electronic conductivity.
- The presence of amorphous Li₂O₂ in close contact with the Cu-THQ cathode can serve as new active surface sites for the product growth and its presence near to next to redox mediator can facilitate a lower and stable oxidation overpotential during the charge process

Investigation of the effect of adding electronic conductivity to a Cu-THQ MOF on Li-O₂ battery performance: <u>performance</u>



- The conductive MOF enables the Li-O₂ battery to have sustainable (cycle life) and efficient (small polarization gap) operation with a low charge potential.
- The InBr₃ and LiNO₃ salts were studied last year with other cathodes and provide anode protection and a redox mediator.
- The MOF based battery has an extended lifetime of 300 cycles at a capacity of 1000 mAh/g under a current density of 0.1 mA/cm² and 150 cycles at 2000 mAh/g

Li-O₂ battery using a new binary transition metal dichalcogenide (TMDC) alloy, Nb_{0.5}Ta_{0.5}S₂, for the cathode and a colloidal MnO₂ electrolyte: voltage profiles at 1 mA/cm²

Schematic of Li-O_2 battery with a colloidal MnO_2 electrolyte formed by dissolving small amount (0.1 M) of KMnO4 in 0.1M LiCl, 0.1M LiClO₄, in DMSO/IL



- The large spheres represent ~800 nm MnO₂ particles
- Also present in the electrolyte is redox mediator catalyst (MnO₄^{-/}MnO₄⁻²) formed by reaction of KMnO4 with DMSO
- Cathode in the figure is based on a Nb_{0.5}Ta_{0.5}S₂ catalyst
- MnO₂ coating is shown on the Li anode formed from the MnO2 nanoparticles

Li-O₂ battery using a new TMDC catalyst (Nb_{0.5}Ta_{0.5}S₂) and a colloidal MnO₂ electrolyte: voltage profiles at 1 mA/cm²



- Cell configuration in both cases is 0.1M LiCl, 0.1M LiClO₄, 0.1M KMnO₄ in DMSO/IL with Nb_{0.5}Ta_{0.5}S₂ and current density of 1 mA/cm²
- This configuration enables the operation of a Li-O₂ battery at a current density of 1 mA/cm² and specific capacity ranging from 1000-10,000 mAh/g in a dry air environment with a cycle life of up to 150.
- This is one of the highest rates achieved so far for a Li-O₂ battery

Li-O₂ battery using a new TMDC catalyst (Nb_{0.5}Ta_{0.5}S₂) and a colloidal MnO₂ electrolyte: comparison with Lil electrolyte and MoS₂ catalyst at 0.5 mA/cm² and 5000 mAh/g



- These results are done with other electrolyte components being the same: 1M LiCl, 0.1M LiClO₄, 0.1M KMnO₄ in DMSO/IL
- Results show a large difference in cycling performance at same rate and capacity.

Exploring the reason for high rates for the Nb_{0.5}Ta_{0.5}S₂/KMnO₄ battery



Comparison of cycling performance for different catalyst/electrolyte additive combinations at 0.5 mA/cm² current density with 5000 mAh/g specific capacity from voltage profiles on last slide

- We have explored the reason why the electrolyte and cathode used in this Li-O₂ battery gives longer cycle life at higher rates and capacities than other combinations
- Our studies shows it is the result of synergies between the following functionalities of the materials:
 - Catalyst with faster electron transfer for OER/ORR
 - Good redox mediator additive for electrolyte
 - Amorphous Li₂O₂ contributes to fast charge/discharge
 - Good anode protection contributes to cycle life and fast charge/discharge

$Nb_{0.5}Ta_{0.5}S_2$ catalyst functionality for ORR/OER



High-resolution TEM image and FFT (inset) acquired from a discharged cathode, after its 20^{th} cycle, show crystalline Nb_{0.5}Ta_{0.5}S₂ with a lattice spacing of 3.0 Å.

DFT optimized structure of O_2 (red arrow) at a cathode interface with a DMSO/IL, LiCl, LiClO₄, KMnO₄ electrolyte for (a) MoS₂ and (b) Nb_{0.5}Ta_{0.5}S₂ catalysts

- The $Nb_{0.5}Ta_{0.5}S_2$ catalyst remains stable during operation of the Li-O₂ battery.
- DFT computations indicate that there is a net charge transfer of 1.6 electrons from the Nb_{0.5}Ta_{0.5}S₂ to O₂, which is much larger than the 1.2 electrons transferred from the MoS₂ to O₂ indicating better electron transfer capability for ORR/OER
- These results are consistent with the experimental work functions showing a much smaller one for Nb_{0.5}Ta_{0.5}S₂.

KMnO₄ electrolyte: redox mediator functionality



Cell configuration in both cases is 0.1M LiCl, 0.1M $LiClO_4$, in DMSO/IL with $Nb_{0.5}Ta_{0.5}S_2$ catalyst and current density of 0.1 mA/cm^2

- For KMnO₄ the charge potential is below 3.7 V vs Li/Li+ at 80 cycles whereas for LiTSI it is above 4.2 at 80 cycles
- These results suggest that KMnO₄ is serving as a redox mediator to lower the charge potential. This
 is the first report of an oxide serving as a redox mediator in a Li-O₂ battery

KMnO₄ electrolyte: redox mediator functionality

The oxidation potential of MnO₄⁻² is ~3.5 V (vs Li/Li⁺) and, thus, could serve as a redox mediator with the oxidation reaction being

 $MnO_4^{-2} \rightarrow MnO_4^{-1} + e^{-1}$

The resulting MnO₄⁻ can serve as an oxidizer during the charge of the solid lithium peroxide [(Li₂O₂)_s] in a two-step process:

$$MnO_{4}^{-} + (Li_{2}O_{2})_{s} \rightarrow MnO_{4}^{-2} + (Li_{2}O_{2} - LiO_{2})_{s} + Li^{+}$$

 $\mathsf{MnO_4^-} + (\mathsf{Li_2O_2}\text{-}\mathsf{LiO_2})_{s} \to \mathsf{MnO_4^{-2}} + \mathsf{O_2} + (\mathsf{Li_2O_2})_{s} + \mathsf{Li^+}$



KMnO₄ electrolyte: redox mediator (RM) functionality



a/

Final

DFT calculations for Lil3 as a RM showing Li cation being removed from Li2O2 surface after reaction with Lil3

DFT calculations for $KMnO_4$ as a RM showing Li cation moving away from Li_2O_2 surface after reaction with MnO_4^{-2}

- The results of the simulation indicate that the Li migrates from the Li₂O₂ surface without any barrier in the presence of KMnO₄. The final state has energy lower than the initial state by 1.4 eV.
- In our previous similar study for the redox mediator of Lil, the Lil₃ has a barrier of ~0.5 eV for the first step in the decomposition of Li₂O₂. (*J. Power Sources* 491, 229506 (2021))

• Therefore, KMnO₄ is more effective as a RM than Lil, consistent with the longer cycle life with the latter.

Amorphous Li₂O₂ contributes to fast charge/discharge



Low-resolution TEM image of the discharged cathode shows Li_2O_2 formation and its interface with the $Nb_{0.5}Ta_{0.5}S_2$ catalyst.



High-resolution image (and its corresponding FFT in inset) showing nanocrystalline Li_2O_2 with crystalline grains sparsely distributed within amorphous Li_2O_2 .

- TEM image reveals the presence of Li₂O₂ is nanocrystalline with Li₂O₂ grains embedded in amorphous Li₂O₂. Amorphous Li₂O₂ has previously been shown to have good electronic conductivity.
- The presence of amorphous Li₂O₂ in close contact with the Cu-THQ cathode can serve as new active surface sites for the product growth and its presence near to next to redox mediator can facilitate a lower and stable oxidation overpotential during the charge process

Anode protection: symmetric cell tests





Long-term cycling performance o, ymmetrical Li||Li cells with the $KMnO_4$ prepared electrolyte and the electrolyte prepared without $KMnO_4$ at 0.5 and 1 mA.cm⁻² current densities, respectively.

Rate-capability of symmetrical Li||Li cell (with KMnO4) at different current densities.

- Results indicate stable and long cycling performance (~1400 hours) with low overpotentials, 25mV and 50mV for 0.5mA/cm² and 1mA/cm², respectively.
- The cells without KMnO₄ fail at a relatively early stage <200 hours with high overpotentials (150mV and 200mV) for 0.5mA/cm² and 1mA/cm², respectively.
- This provides evidence on the dual functionality of KMnO₄ as both RM and anode protector.

Characterization of anode coating from the MnO₂ colloidal electrolyte



- A combination of TEM-EDX, XPS, and EELS was used to analyze the SEI on the Li anode
- Results indicated that it was predominantly MnO₂ deposited from the colloidal MnO₂ electrolyte
- From EELS the valency of Mn was found to have an average value of 3.01 over the mapped region. The average valency of 3.01 implies the formation of a LiMnO₂ like SEI layer with the Li coming from Li ion transport through the coating.

DFT simulations of MnO₂ coating



Initial and final structure of α -MnO₂/Li interface from ab initio molecular dynamics (AIMD) calculations. The purple, red and green spheres represent the Mn, O and Li atoms.

- This AIMD simulation reveals mixing between Li and MnO₂, as shown in the final structure. The radial distribution function (not shown) for the Li-Mn and Li-O bonds reveals the formation of these bonds in the interface region consistent with the formation of LiMnO₂
- The simulation reveals that the diffusion coefficient (D) of Mn and O atoms are similar within this system, while Li has a larger D value indicating that there will be favorable Li transport within the MnO₂ layer consistent with the findings of the excellent rate-capability of symmetrical LillLi cell.

Summary: High rates for the Nb_{0.5}Ta_{0.5}S₂/KMnO₄ battery



Our studies shows high rates are the result of synergies between the following functionalities of the materials:

- Catalyst with faster electron transfer for OER/ORR
- Good redox mediator additive for electrolyte
- Amorphous Li₂O₂ contributes to fast charge/discharge
- Good anode protection contributes to cycle life and fast charge/discharge

Proposed Future Work

- Based on our successes in the past year, we will develop Li-O₂ batteries that can operate in a realistic air atmosphere with a low charge potential, high rate, and a long cycle life.
- Complementary strategies will be used.
 - The first will be systematic studies of new bifunctional additives to find ones that protect the Li anode, are stable, and enable easy decomposition of the discharge product for fast charge/discharge. We have preliminary results on a SnX₂ (X=I, Br) additive that are very promising
 - Modify the solvent to increase stability for higher rates
 - Explore the use of colloidal electrolytes of different compositions
- The second will be use of electrospinning or 3-D printing techniques to make high surface area of cathode based on our TMDC catalyst to greatly increase energy density.

Remaining Challenges and Barriers

- The major challenge remains the discovery of electrolytes that work in combination with transition metal dichalgonide catalysts that can operate effectively in an air environment with high charge rates and higher capacities
- A second major challenge is to assess and optimize the Li-O2 lab scale batteries to be able to have practical applications outside the lab, which will be a future goal for this work.

Collaborations with other institutions and companies

- A. Subramanian (UIC)
 - TEM studies of SEI of Li anodes and discharge product on cathodes
- J. G. Wen (ANL)
 - TEM studies of SEI of Li anodes and discharge product on cathodes
- Badri Narayanan (University of Louisville)
 - Machine learning for potentials for classical MD simulations
- F. Khalili-Araghi, UIC
 - Classical molecular dynamics simulations of bulk electrolytes
- Z. Huang, Stockholm University
 - MOFs

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